SELENIUM DATA

(REVISION OF INFORMATION CIRCULAR 7690)

BY J. D. SARGENT

* * * * * * * * * * Information Circular 7715

UNITED STATES DEPARTMENT OF THE INTERIOR
Douglas McKay, Secretary
BUREAU OF MINES
J. J. Forbes, Director

Work on manuscript completed January 1955. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Information Circular 7715."

April 1955

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J. D. Sargent[1]/

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INTRODUCTION

Selenium might be described as a paradoxical element, being either a metal or a nonmetal, a conductor or nonconductor, amorphous or crystalline, colorant or decolorant, and a hydrogenator or dehydrogenator.

Selenium was discovered in 1817 by the Swedish chemist, Berzelius, while studying flue dust from the lead chambers of the sulfuric acid works at Gripsholm, Sweden,

The ordinary stable form of selenium is a crystalline, grayish solid with semimetallic luster. It melts at 217° C., boils at 684.8° C., and has a density of 4.79.

Selenium is closely related to sulfur, with which it is commonly associated in nature. It is found native, like sulfur, and also in the selenides of copper, silver, lead, mercury, bismuth, and thallium. About 25 minerals contain selenium in varying percentages, but none of the species is considered a commercial source. (See Appendix A.)

The commercial source of selenium at present is the anode mud or slime produced in the electrolytic refining of blister copper. The selenium content of blister copper anodes handled by domestic refineries ranges from 0.01 to 0.07 percent; the slimes generally contain 4 to 25 percent selenium. (See Appendix F.)

Commercial uses for selenium began to develop on a substantial scale during the interwar period in the glass, ceramic, chemical, pigment, and rubber industries, and later in the stainless steel industry. Selenium rectifiers for converting alternating current to direct current were used industrially for many years but only on a small scale. In 1947 the miniature-type selenium rectifier for electronic circuits was developed. These diminutive rectifiers, as employed in voltage multiplier circuits for radio and television sets, eliminate heavy and bulky transformers and rectifier tubes. Military uses of the selenium rectifier cover a wide range.

Selenium is used in the glass industry as a decolorizer and in the stainless steel industry as an additive to improve machinability and to control the quality of castings. A diversified group of chemical uses, including pigments and rubber accelerators, now consumes more selenium than the glass industry and the steel industry combined.

Domestic production of primary selenium from 1947 to 1951 averaged 514,988 pounds annually and was produced by 3 companies: American Smelting & Refining Co., U. S. Metals Refining Co. (subsidiary of American Metal Co., Ltd.), and International Smelting & Refining Co. Primary selenium production in the United States was 687,384 pounds in 1952 and 923,887 pounds in 1953, produced by the aforementioned companies and Kennecott Copper Corp. (see Appendix E). Demand existed for larger quantities of selenium than were available.

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PHYSICAL AND CHEMICAL PROPERTIES

Selenium chemically resembles sulfur and like sulfur has several allotropic forms. Many of the allotropic forms can be grouped together and called reddish-brown selenium precipitates. The lightest of the reddish-brown allotropics has a specific gravity of 4.3 and softens at 60° C. Another of the reddish-brown allotropics is colloidal and fluoresces in water. Vitreous selenium is purple-black and can be formed by cooling the reddish-brown allotropics quickly. Slow heating the vitreous form to 65° C. or over will convert selenium to its most common form, silvery-gray metallic selenium. Hexagonal acicular crystals of metallic selenium are sometimes hollow and flexible, with a Moh's hardness of 2 and a melting point of 217° C. Selenium boils at 684.8° C., giving off dark-red vapors, and at higher temperatures it will sublime, emitting yellowish vapors. Optically, metallic selenium is pleochroic and anisotropic with an "O" index of 3.0 and an "E" index of 4.04. Electrically, selenium is a photoelectric semiconductor. (See Appendix B for selenium atomic data.)

The chemical nature of selenium is apparent in the chemical usage of selenium and selenium compounds outlined under Usage in this circular.

GEOLOGY AND MINERALOGY

The selenium content of igneous rocks is about 0.09 p.p.m. Cores of marine sediments from the Continental Shelf average 1 to 2 p.p.m. selenium, whereas deep sea cores assay much lower (56).2/ Selenium assays of the Continental Shelf deposits correspond closely with the selenium content of the sedimentary rock strata of Western United States and the soils derived from them (177).

A large area of North America - from Canada to Mexico and from the Mississippi to the Rocky Mountains - is underlain by seleniferous rocks and soils. Most of the seleniferous rocks are sedimentary formations ranging in age from the late Paleozoic era to the present. Rocks formed during the Cretaceous period have been found to be the most highly seleniferous. Limonitic concretions from the Cretaceous Niobrara formation contain from 20 to over 500 p.p.m., whereas the surrounding shales contain only 2 p.p.m. Phosphate rock from the Permian Phosphoria formation of western Wyoming was found to vary from 1 to 600 p.p.m. For a list of seleniferous formations, see Appendix C.

Soils derived from seleniferous rocks usually contain 2 or 3 p.p.m. selenium. Annual rainfall in the seleniferous area is not sufficient to leach even the more soluble compounds of selenium from the soil. Soils containing only 1 or 2 p.p.m. selenium commonly sustain plants with a selenium content of 50 to 10,000 p.p.m. and in one instance a record 14,920 p.p.m. Some plants are indicative of seleniferous soils. For a list of selenium indicator plants and their distribution, see Appendix D.

Aside from the selenium minerals themselves, magnetic sulfide deposits represent the greatest known concentration of selenium in the earth's crust. Average selenium content of magnetic sulfides is about 0.02 percent. A list of selenium minerals appears in Appendix A.

2/ Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

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GEOGRAPHIC DISTRIBUTION AND FOREIGN PRODUCTION

Central and South America

Chili ranks second only to the United States as a copper producer but apparently produces no selenium or commercial products from which selenium is recovered in substantial amounts. Many occurrences of selenium minerals are reported from Argentina, Bolivia, Chile, and Honduras. None of these occurrences are known to be very extensive.

Africa

Northern Rhodesia and the Belgian Congo are also major producers of copper. Copper anodes from Rhodesian copper refineries assay 0.0141 percent selenium, and their slimes assay 12.64 percent selenium. Northern Rhodesia produced about 30,000 pounds of selenium in 1952. Much of this selenium is recovered in Belgium and reported as Belgian production.

Australia

Selenium is produced in Australia by the Electrolytic Refining & Smelting Co. of Australia Pty., Ltd., Port Kembla, from the company's own anode muds and from those obtained from the Mount Lyell Mining & Railway Co., Queenstown, Tasmania. Australian production of selenium is about 4,000 pounds a year from slimes containing only 1 or 2 percent selenium. Mount Morgan, Queensland, blister copper contains 0.019 percent selenium, but no recovery has been recorded.

Asia

Selenium is recovered at the following Japanese copper refineries: Furukawa Electric Co., Ltd., Nikko, Tochigi Prefecture; Nippon Mining Co., Ltd., Hitachi, Ibaragi Prefecture; Mitsubishi Metal Mining Co., Ltd., Osaka, Osaka Prefecture; Mitsui Mining and Smelting Co., Ltd., Takehara, Hiroshima Prefecture; Sumitomo Metal Mining Co., Ltd., Niihama, Ehime Prefecture; Nippon Mining Co., Ltd., Saganoseki, Oita Prefecture and from the following sulfuric acid plants: Ishihara Mining Co., Ltd., Yokkaichi, Mie Prefecture; and Koatsu Mining Co., Ltd., Omuta, Fukuoka Prefecture. In addition, the Republic Chemical Corporation of Tokyo initiated selenium recovery in September 1952. Japan produces about 50,000 pounds of selenium annually.

U. S. S. R.[3/]

Soviet Union selenium statistics have not been available since 1940. A review of what little information was available before that time is presented here:

During 1926-27 the U. S. S. R. consumed about 2,000 pounds of selenium a year, only one-third of which was produced in that country. U. S. S. R. annual selenium production potential during this period was estimated to be 6,000 pounds.

Russia produced 5,000 pounds of selenium in 1931 from electrolytic slimes and was preparing to recover selenium from sulfuric acid production byproducts in 1932.

3/ Based on information contained in Bureau of Mines files and from an unpublished manuscript by Alexander Gakner of Falls Church, Va.

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Selenium content of 7 percent has been recovered from the Kyshtym electrolytic slimes since 1928, and recovery exceeded 2,000 pounds per year by 1934. A Moscow electrolytic plant, with a potential production of 4,000 pounds of selenium per year from 4-percent selenium slimes, was completed in 1935. Selenium has also been recovered from Cottrell-precipitator dusts at a super-phosphate plant in Odessa since 1935. Another reference to these same dusts, however, stated that the byproduct recovered was tellurium.

Selenium recovery from the Belovo zinc-lead ores of the Altai region was initiated about 1938.

The United States imported 2,762 pounds of selenium from the U. S. S. R. in 1939 and 11,056 pounds in 1940. No selenium has been imported from the U. S. S. R. since 1940.

Judging from U. S. S. R. copper production in 1953, Soviet selenium production would be about 100,000 pounds per year.

Several seleniferous ores are known to occur in the U. S. S. R. The Karabash, Kalata, and Krasnouralsk copper and pyrite deposits in the Ural Mountains contain as much as 0.025 percent selenium. Ores from Obnovlennyy Rudnik contain 0.14 to 0.24 percent selenium. The Kedabek pyrite deposit in the Caucasus assays 0.0143 percent. The Medredevka barite deposits in the Ural Mountains are reported to be seleniferous.

Europe

Sweden is usually the largest European producer, and during 1951 Swedish selenium output was 90,000 pounds. Most of this production can be attributed to Boliden Gruv AB, operating several mining properties in the Skelleftea region and a smelter and electrolytic refinery at Skellefthawn.

Several Norwegian firms planned to initiate selenium recovery in 1953, and the Outokumpy Oy in Finland produces selenium.

Belgium is a significant selenium producer and exported more than 22,000 pounds in 1951, more than 37,000 pounds valued at $616,240 to 17 foreign countries in 1952, and more than 61,000 pounds valued at $957,080 to 15 foreign countries in 1953. Metallurgie de Hoboken, the major Belgian producer, obtains most of its selenium-bearing ores and slimes from Africa.

Western Germany produced over 16,000 pounds of selenium in 1951; the Norddeutsche Affinerie of Hamburg is the major producer. Much of its selenium raw material is imported from South America.

International Nickel Co. of Canada upgrades selenium at its Clydach refinery near Swansea, Wales, United Kingdom. Production from this plant is included in Canadian statistics.

In southeastern Yugoslavia, the Bor Copper Mining Corp. electrolytic refinery recovers about 1,000 pounds of selenium per year.

In Linate, near Milan, Italy, the Montecatini group recovers selenium from copper sulfate.

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North America

Mexico is a major selenium producer, but most of their selenium is recovered and refined in the United States and is included in the United States production statistics. Blister copper from the Cananea Consolidated Copper Co. at Cananea, Mexico, which was formerly refined in the United States, is now refined at an electrolytic copper refinery near Mexico City and the anode muds are sent to a silver recovery plant at Monterey, Mexico, for extraction of the contained metals.

Selenium is produced in Canada by the International Nickel Co. at Copper Cliff, Ontario, and by Canadian Copper Refiners, Ltd., Montreal East, Quebec. The latter plant, which treats blister copper produced by Noranda Mines, Ltd., and by Hudson Bay Mining & Smelting Co., has a rated annual production capacity of 450,000 pounds of selenium, but its 1950 output was less than 350,000 pounds, after declining gradually from its peak output of 521,867 pounds in 1946 (150, 151). This decline reflects the reduction in output of selenium-rich, high-grade ores from the Horne mines at Noranda and a larger proportion of copper obtained from other mines. The Hudson Bay blister is usually high in selenium, available analyses showing 0.18 percent of this element. The efficiency of selenium recovery at this plant is extraordinarily high. The International Nickel Co. gets most of its selenium-bearing ore from the Sudbury Basin in Ontario, which has an ore reserve containing an estimated 3,000,000 pounds of selenium. The Copper Cliff refinery has a 270,000-pound capacity for selenium production.

The United States is the world's leading producer of selenium.

DOMESTIC PRODUCTION, CONSUMPTION, AND FOREIGN TRADE

The American Smelting & Refining Co. (Baltimore, Md.), United States Metals Refining Co. (Carteret, N. J.), International Smelting & Refining Co. (Perth Amboy, N. J.), and Kennecott Copper Corp. (Garfield, Utah) are the principal selenium producers in the United States. In addition, several companies such as Kawecki Chemical Co., Boyertown, Pa.; and Vickers Electric Division, Vickers, Inc., St. Louis, Mo., recover selenium from scrap of rectifier manufacturers and spent catalysts and also upgrade commercial-grade selenium into high-purity selenium. In 1953 the Kawecki Chemical Co. initiated selenium recovery from sulfuric acid-production byproducts.

Domestic production of selenium from 1947 to 1951 averaged 514,988 pounds annually. Total 1952 primary selenium production was 687,384 pounds, and 66,781 pounds of secondary selenium were recovered. A total domestic primary selenium production of 923,887 pounds and 97,948 pounds of secondary production was attained in 1953. A goal of 1,100,000 pounds of domestic selenium production was set for 1955.

Apparent domestic consumption (producers' domestic shipments plus imports to consumers) of selenium has ranged during the 5 years from about 600,000 to over 1,000,000 pounds, averaging 848,460 pounds annually. Producers' domestic shipments in the period averaged 536,215 pounds and imports to consumers 312,245 pounds. The trend since this period has been toward greater domestic shipments and lesser consumer imports. Apparent domestic consumption of selenium in 1952 was 802,033 pounds and 1,125,501 pounds in 1953. Demand in the 1951-52 period for selenium and selenium compounds exceeded 1,500,000 pounds and was steadily increasing, with no hope of fulfillment in the foreseeable future.

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Exports of selenium by producers were at a low level during the 1947-51 period, averaging 27,321 pounds annually. Exports since this period have been at an even lower level and under strict Government control.

Imports of selenium from 1947 to 1951 averaged 315,568 pounds per year. A record 529,175 pounds of selenium was imported in 1947, largely from Canada. Total selenium imports in 1952 were only 123,135 pounds and 99,865 pounds in 1953.

The National Production Authority placed both imported and domestically produced selenium under complete allocation in February 1952, explaining that the action was necessary if essential defense requirements were to be met. Allocation was terminated in early 1953, but the shortage continues.

The outlook is not favorable under a continuation of existing circumstances for obtaining increased supplies of selenium from the usual sources to meet expanding requirements or to provide for full mobilization needs.

METALLURGY

Blister copper averages about 0.05 percent selenium. About 25 percent of the selenium content of copper ores has been lost before the blister copper stage is reached. Blister copper is converted to refined copper by electrolysis. Anode muds or slimes are a byproduct of this electrolytic refining. Anode slimes contain from 2 to 25 percent selenium, averaging about 8 or 9 percent. The recovery of selenium from anode slime is different at each individual plant.

Tyler's selenium report (178) summarizes several selenium-recovery processes that have been used as follows:

(a) Oxidizing roast: Shallow layers of slimes are heated to 500° to 800° F. with plenty of air. Some selenium and arsenic are volatilized. The calcine is leached with H_2SO_4, foul electrolyte, or liberator solution, and the solution sent to the electrolytic department. Selenium is precipitated as copper selenide in the liberator system but is easily recovered.

(b) Sulfating roast: Concentrated sulfuric acid is added to the slimes before charging, or during the roast, by spraying. Selenium and tellurium are oxidized to the corresponding oxides or oxysulfates. Roasting at high temperature drives off selenium dioxide, but too high temperaatures (over about 1,200° F.) tend to decompose copper sulfate. Roasted slimes are leached with hot water. The leach liquor contains silver and some selenium and tellurium, all of which are precipitated by cementation with metallic copper or raw slimes. Selenium requires a somewhat longer concentration time than silver, and tellurium is even more resistant to cementation than selenium.

(c) Boiling with dilute H_2SO_4 and niter: This process is of only historical interest owing to high chemical cost, fume disposal problems, impure solutions, excessive corrosion of equipment, and other disadvantages.

(d) Aeration in dilute H_2SO_4: A suspension of slimes in hot dilute H_2SO_4 is blown with air. This dissolves metallic copper and leaves selenium and tellurium in the slimes, along with gold and silver. This process is economical of acid, but this is partly offset by the cost of steam. Equipment is simple but bulky, and corrosion problems are not serious.

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(e) Pyrometallurgical methods: Direct smelting of slimes has been virtually abandoned, as have various attempts to treat selenide matte in small converters or tank furnaces. The sodium bisulfate process recently adopted by Kennecott, however, is in this category. Soda smelting is a pyrometallurgical method, but in commercial practice the raw slimes are first decopperized by acid leaching or some other method.

(f) Miscellaneous methods: A number of methods have been proposed for treating raw slimes, including aeration in aqueous solutions of ammonia, etc., aeration in aqueous cyanides, chlorination, and treatment with manganese dioxide and H_2SO_4. None of these methods, however, have proved commercially feasible.

The sulfate roast process was used by the Canadian Copper Refiners, Ltd., of Montreal East, Quebec.

The American Smelting & Refining Co. utilized the soda-smelt process for many years at Baltimore. The nature of recent process changes at this plant has not been disclosed.

Kennecott Copper Co. fused selenium slimes with sodium bisulfate after first leaching out copper with acid.

The Perth Amboy, N. J., plant of the International Smelting & Refining Co. converted aerated slimes to alkaline slags. The selenium content of these slags was dissolved with sulfuric acid and then acidified with hydrochloric acid. Elemental selenium was then precipitated with sulfur dioxide.

At the Copper Cliff, Ontario, refinery, International Nickel Co., the slimes, were first fluxed with sand and fluorspar. The resulting matte was refined to doré and the soda niter slags were leached with water. Selenium was recovered from this leach water by precipitation as "coke" selenium.

In some plants, slimes and fume products from other metal-refining operations are added to the byproducts-recovery processes along with selenium scrap and spent selenium catalysts. In addition, many fractions are recycled and reprocessed, the net result being a rather complicated operation. Since these raw materials are seldom assayed, the source of any given batch of selenium is unknown.

Slime-treatment processes are primarily designed to recover the precious metals. Selenium and tellurium recovery are of secondary importance. Frequent changes are made in slime treatment processes to increase recovery rates, lower costs, and accommodate changes of raw materials.

The selenium end product of all of these processes is commercial-grade selenium (97.2 to 99.94 percent pure) usually in coke form. This coke selenium in pulverized and sold as commercial-grade selenium or further refined to high-purity selenium (99.99+ percent). Ferroselenium can be produced as a byproduct of high-purity selenium production. Ferroselenium is used directly in the production of stainless steel.

In 1953 selenium-production facilities were sufficient for much larger operations had an increased supply of slimes become available.

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USAGE (152, 183)

Before World War I, selenium was regarded as the abomination of the smelterman and was discarded. Even with the present strong demand, selenium is regarded of minor importance as compared with precious-metal byproducts. During that war, when manganese was in short supply, selenium first came into use as a substitute to decolorize glass by neutralizing the greenish tinge imparted by iron impurities. Inasmuch as selenium has certain inherent advantages over manganese in the decolorization of glass, its use continued after manganese again became available.

The glass industry continued to be the major consumer of selenium until after World War II, when the selenium-rectifier industry became the principal consumer. Selenium rectifiers have been known since 1884 but were not used extensively until about 1930, when German and American investigators improved the device. Selenium dry-plate rectifiers change alternating to direct current and are extensively used in electroplating, welding, direct current motor operation, battery chargers, magnet coils, arc lamps, induction braking, and electrostatic precipitation. Additional military uses of selenium rectifiers include aircraft controls, degaussing equipment, dynamotor power, guided missles, ground starters for aircraft, magnetic amplifiers, radar equipment, relay and solenoid power, sonar equipment, telephones, teletypes, and voltage regulators. The largest increase in rectifier use occurred in 1947, when miniature rectifiers suitable for radio and television circuits were developed. These diminutive rectifiers, used in voltage multiplier circuits of radio or television sets, can deliver 200 to 500 volts d.c. from a 117-volt a.c. source, eliminating a heavy and bulky transformer and rectifier tube and saving more than 1/2 pound copper and 7-1/2 pounds of steel per television set. (See fig. 1.)

Selenium has photoelectric conductivity, as well as rectification properties. Selenium photoelectric cells are used in photographic exposure meters, electric eyes, colorimeters, and pyrometers.

As previously noted, selenium is added to glass to alter the greenish tinge of iron impurities to a neutral gray. From 0.02 to 0.3 pound of metallic selenium, sodium selenite, barium selenite, or sodium selenate per ton of glass is required, the exact quantity being determined by the iron content to be neutralized. Excess selenium causes a pink tinge, which is desirable in the case of milk bottles and a few other food-containers. From 1 to 50 pounds of selenium per ton of glass yields a very desirable ruby-red glass, which is used in tableware, taillight-signal lenses, light filters, infrared equipment, lantern globes, and traffic lights.

Selenium is important in the rubber industry. Added mostly in the form of selenium diethyl dithiocarbonate, selenium acts as an accelerator and vulcanizing agent and, in addition, promotes resistance to heat, oxidation, and abrasion and increases the resilience of rubber.

Selenium as sulfoselenide is used as a pigment to produce orange, red, and maroon colors in paint, soap, rubber, ceramics, paper, printing inks, plastics, dyes, leather, and other products.

Selenium and its compounds are widely employed in industrial and research chemistry. Selenium dioxide oxidizes organic compounds, producing reactions not obtainable by any other known method. Selenium can be either a hydrogenating or dehydrogenating agent. Occasionally, 10 times as much selenium as organic compound is required during dehydrogenation. Selenium is a hydrogenation and cracking

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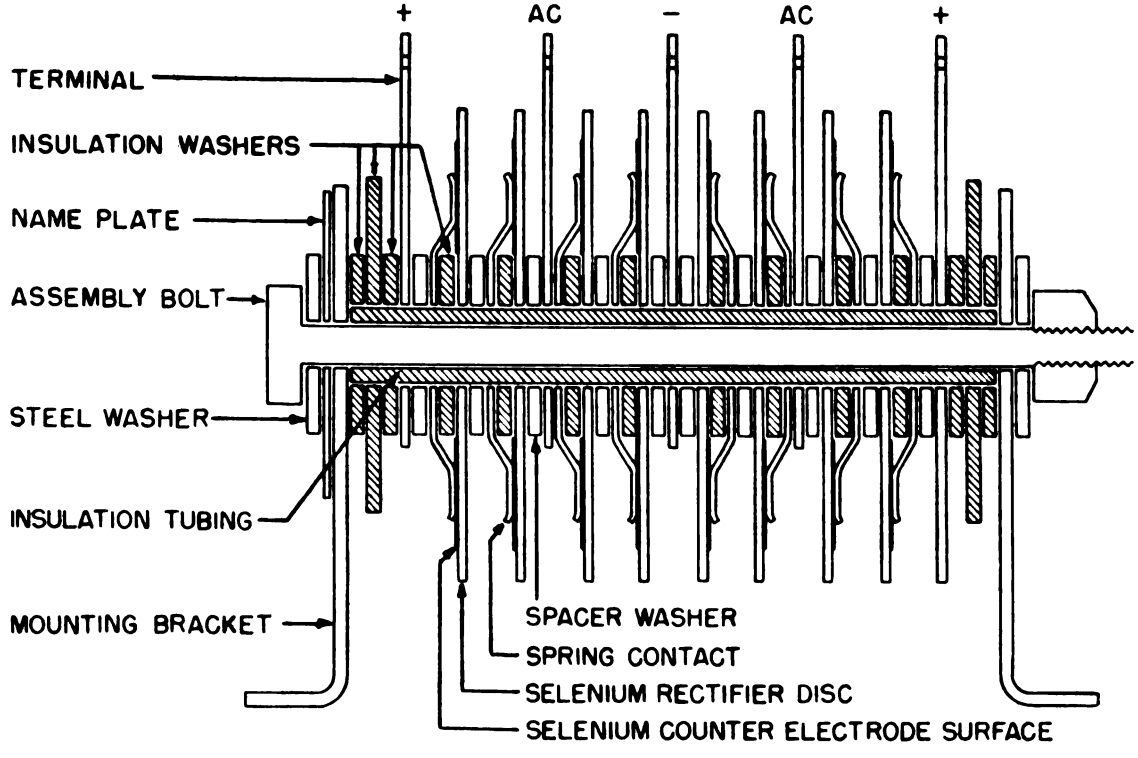

Figure 1. - Cut-away view of typical rectifier stack assembly.

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catalyst in crude oil and coal distillations. Soaps, waxes, edible fats, and plastics are produced by fat hardening with a selenium catalyst. The Kjeldahl method of nitrogen determination utilizes a selenium catalyst. It imparts exceptional antioxidant properties to printing ink, mineral oils, transformer oils, and vegetable oils. Nondrying properties of linseed, oiticica, and tung oils are due to selenium. Selenium also retards gelation in tung oil. The antioxidant and antigalling properties of selenium compounds find application in lubricating oils and in extreme pressure lubricants. Selenium is the catalyst that synthesizes cortisone, used to treat arthritis, and isonicotinic acid, used to treat tuberculosis. Selenium compounds are found in dandruff, dermatitis, and deodorant pharmaceuticals. Selenium compounds are finding wide application as insecticides, fungicides, parasiticides, bactericides, and herbicides. Photographic photosensitizers and toning baths contain selenium compounds such as sodium selenosulfate. Blasting caps, mercury vapor detectors, flotation reagents, fireproofing agents, insect repellants, phosphorescents, and luminescents can be made from selenium compounds.

Care must be exercised in such widespread usage, inasmuch as selenium and most of its compounds are toxic or corrosive. Selenium oxychloride is so corrosive that it is known as the universal solvent.

Selenium improves the machinability of stainless steel. Forging steels contain 0.18 to 0.22 percent selenium and the full machining grade 0.30 to 0.35 percent. In cast steel 0.01 percent to 0.05 percent selenium assures a fine-grained, bubble-free casting. Small quantities of selenium improve machinability and tensile strength of copper and copper-rich alloys without appreciably lowering ductility or conductivity.

Xerography, a dry photographic process, employs selenium-coated metal disks from which the photographic image is transferred by static electricity.

Radioactive selenium has been utilized in radiography.

Percentagewise, the electrical industry and the chemical industry each consumed about 40 percent of this Nation's selenium. The glass industry used about 13 percent of the total available supply, and the steel industry consumed the remaining 7 percent.4/ In 1954 the electrical industry consumed more than half of the selenium produced.

APPENDIX A

Selenium Minerals

Native selenium - Se
Selen-tellurium - (Se, Te)
Selenium sulfur - (Se, S)
Aguilarite - $Ag_2(Se,S)$
Naumannite - Ag_2Se
Berzelianite - Cu_2Se
Crookesite - $(Cu,Tl,Ag)_2Se$
Eucairite - CuAgSe
Umangite - Cu_3Se_2
Clausthalite - PbSe
Tiemannite - HgSe
Paraguanajuatite - $Bi_2(Se,S)$
Eskeborite - FeSe(?)
Klockmannite - CuSe
Guanajuatite - Bi_2Se_3
Penroseite - $(Ni,Cu,Pb)Se_2$
Wittite - $Pb_5Bi_6(S,Se)_{14}$
Weibullite - $PbBi_2(S,Se)_4$
Platynite - $PbBi_2(Se,S)_3$
Selenolite - SeO_2
Ahlfeldite - $Ni(SeO_3) .6H_2O$
Chalcomenite - $CuSeO_3.2H_2O$
Cobaltomenite - $CoSeO_3.2H_2O$
Kerstenite - $PbSeO_3.2H_2O$ (?)
Molybdomenite - A lead selenite

4/ Derived from statistics supplied by the Bureau of the Census for 1952.

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Other minerals that occasionally contain isomorphic or interstitial selenium are native tellurium, melonite, lillianite, emmonsite, metacinnabar, chiviatite, vaesite, and many sulfides and sulfosalts, especially those containing iron and copper.

An unnamed Co-Ni-Cu selenide is described by Robinson and Brooker[5] and an unnamed $PbSeO_4$ by Goni and Guillemin.[6]

APPENDIX B

Selenium

Chemistry and Physics[7]

Atomic number: 34 Period: IV Group: VI

Atomic weight: International atomic weight in 1925, 79.2; changed to 78.96 in 1949. Isotope abundance as follows:

Se^{74} - 0.87, Se^{76} - 9.02, Se^{77} - 7.58, Se^{78} - 23.52.

Se^{80} - 49.82, Se^{82} - 9.19.

Valence: 2, 4, or 6.

Electronic configuration: 34 electrons in 4 shells as follows:

K		L			M				N		
1		2			3				4		
S	S	P	S	P	D	S	P	D	F		
2	2	6	2	6	10	2	4				

Radiation of isotopes: Artificially radioactive.

Isotope	Type of radiation	Half-life	Radiation energy (MEV) Particles	Rays
Se^{70}	B^+	44 min.		
Se^{72}	K	9.5 days		
Se^{73}	B^+, K	6.7 to 7.1 hr.	1.29	
Se^{75}	K, gamma, e^-	115 to 127 days		0.77 to 0.5
Se^{77m}	I.T., gamma	17.5 sec.	.135e^-	.15
Se^{79m}	I.T., e^-	3.9 min.		.096
Se^{79}	B^-	6×10^4 yr.	.16	
Se^{81m}	I.T., e^-	57 to 59 min.		.099
Se^{81}	B^-	17 to 19 min.	1.5	
Se^{83m}	B^-, gamma	67 sec.	3.4	
Se^{83}	B^-, gamma	25 to 30 min.	1.5	.017 to 1.1
Se^{84}	B^-	2.5 min.		

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Stable isotopes: Se^{74}, Se^{76}, Se^{77}, Se^{78}, Se^{80}, Se^{82}
U^{235} fission products: Se^{79}, Se^{81m}, Se^{81}, Se^{83m}, Se^{83}, Se^{84}
Polarizability of the free anion of selenium = 112 x 10^{25}

APPENDIX C

Seleniferous Formations[8]

Tertiary

Fort Union formation, Tuscher formation, Wasatch formation, Wind River formation, Bridger formation, Uinta Mountain group, Duchesne River formation, Chadron formation, Arikaree group (formation), Browns Park formation, North Park formation.

Cretaceous

Cloverly formation, Gannett group, Thermopolis shale, Dakota sandstone (quartzite west of Front Range, sandstone east of Front Range, formation in Kansas and Minnesota, group in and to the northeast of the Front Range), Aspen shale, Mowry shale, Mancos shale, Frontier formation, Carlile shale, Niobrara formation, Hilliard formation, Steele shale, Iles formation, Williams Fork formation, Lewis shale, Pictured Cliffs sandstone, Fruitland formation, Kirtland shale, McDermott formation, Lance formation, Medicine Bow formation, Mesaverde formation.

Jurassic (?)

Bear River formation.

Jurassic

Wingate sandstone, Kayenta formation, Curtis formation, Sandance formation, Summerville formation, Morrison formation, Gannett group.

Triassic

Dinwoody formation, Moenkopi formation, Chugwater formation, Chinle formation.

Permian

Supai formation, Cutler formation, Phosphoria formation, Chugwater formation.

Permian (?)

Rico formation.

Pennsylvanian

Amsden formation, Paradox member, Hermosa formation.

8/ Modified from Trelease, S. F., and Beath, O. A. (177).

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APPENDIX D

Selenium Indicator Plants[9/]
(See fig. 2.)

Astragalus

Species	Distribution
Astragalus bisulcatus (Hook.) (Gray)	Alba., Sask., Man., Mont., N. Dak., Idaho, Wyo., S. Dak.; Nebr., Colo., Okla., Kans., N. Mex.
A. diholcos (Rydb.) (Tidestrom)	Wyo., Colo.
A. haydenianus (Gray)	Wyo., Utah, Colo., Nev., N. Mex.
A. oocalycis (Jones)	Colo., N. Mex.
A. racemosus (Pursh)	Alba., Mont., N. Dak., Wyo., S. Dak., Nebr., Utah, Colo., Kans., N. Mex. Okla., Tex.
A. osterhouti (Jones)	Colo.
A. albulus (Woot. & Stand)	Ariz., N. Mex.
A. argillosus (Jones)	Utah, Ariz.
A. confertiflorus (Gray)	Wyo., Utah, Colo., Ariz., N. Mex.
A. confertiflorus var. flaviflorus (Kuntze) (Jones)	Wyo., Utah, Colo.
A. moencoppensis (Jones)	Utah, Ariz.
A. grayi (Parry)	Wyo., Mont.
A. pectinatus (Dougl.)	Alba., Sask., Man., Mont., N. Dak., S. Dak., Utah, Wyo., Colo., Kans.
A. pectinatus var. platyphyllus (Jones)	Wyo.
A. toanus (Jones)	Idaho, Utah, Nev.
A. beathii (Porter)	Ariz.
A. eastwoodae (Jones)	Utah
A. ellisiae (Porter)	N. Mex.
A. crotalariae (Benth.) (Gray)	Calif., Nev., Ariz.
A. pattersoni (Gray)	Utah, Colo., Ariz., N. Mex., Tex.
A. pattersoni var. praelongus (Sheld.) (Jones)	Nev., Utah, Ariz., N. Mex.
A. preussii (Gray)	Nev., Utah, Calif., Ariz., N. Mex.
A. recedens (Jones) n. comb.	Colo., N. Mex.
A. sabulosus (Jones)	Utah, Ariz.

Xylorrhiza

Xylorrhiza glabriuscula (Nutt.)	Colo., S. Dak., Wyo.
X. parryi (Gray) (Greene)	Wyo.
X. venusta (Jones) (Heller)	Utah, Colo.
X. tortifolius (Gray) (Greene)	Ariz., Calif.
X. villosa (Nutt.)	Colo.

Oonopsis

Oonopsis argillacea (A. Nels.)	Wyo., S. Dak.
O. condensata (A. Nels.)	Wyo.

9/ Modified from Trelease, S. F., and Beath, O. A. (177).

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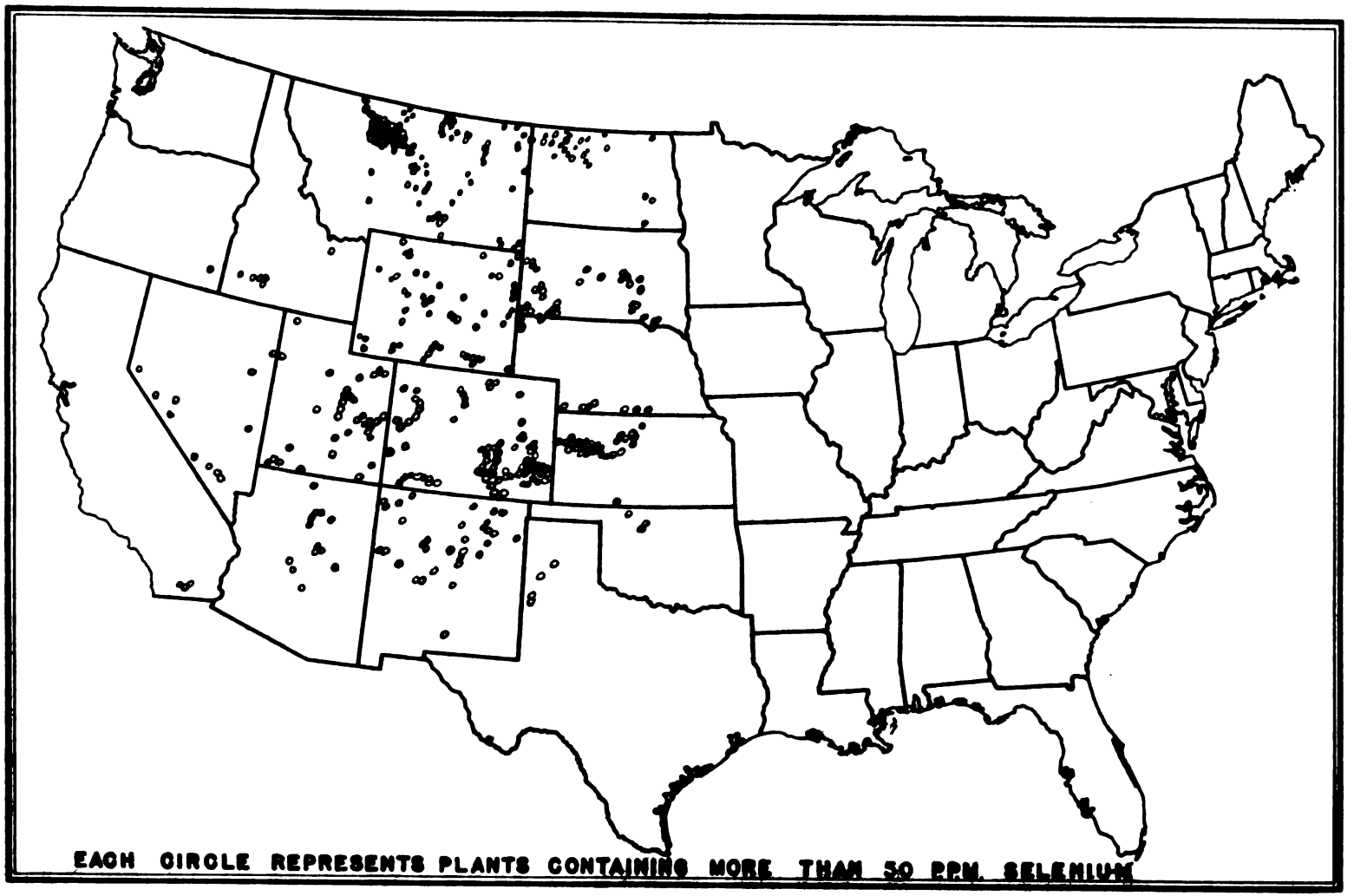

Figure 2. - Distribution of seleniferous vegetation. *(Modified from Trelease, S. F., and Beath, O. A. (177).)*

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Oonopsis (Con.)

Species	Distribution
O. monocephala (A. Nels)	Colo.
O. engelmannii (Gray) (Greene)	Colo., Kans.
O. foliosa (Gray) (Greene)	Ala.
O. wardii (Gray) (Greene)	Wyo.

Stanleya

Stanleya albescens (Jones)	Colo., Ariz., N. Mex.
S. pinnata (Pursh) (Britt.)	Utah, Wyo., S. Dak., N. Dak., Kans., Ariz., Calif., Colo., Mont., Idaho, Nev., N. Mex., Tex.
S. tomentosa (Parry)	Wyo.
S. vividiflora (Nutt.)	Mont., Ore., Idaho, Wyo., Nev., Utah

Several other species of Xylorrhiza, Oonopsis, and Stanleya may be selenium concentraters as well as some species of Aster, Atriplex, Castilleja, Grayia, Grindelia, Gutierrezia, Machaeranthera, Mentzelia, and Sideranthus.

APPENDIX E

Salient statistics of elemental selenium in the United States, 1940-53, in pounds[1]

(See fig. 3)

Year	Production[2]	Primary producers: Domestic shipments	Primary producers: Stocks at end of year	Imports[3]: Pounds	Imports[3]: Value
1940	328,731	330,207	178,873	134,429	$198,163
1941	620,493	661,171	105,026	197,873	288,161
1942	502,396	442,482	174,803	83,666	127,004
1943	643,660	613,434	225,828	81,720	142,032
1944	525,331	394,818	379,137	97,800	170,582
1945	486,815	554,944	324,967	216,793	395,934
1946	298,233	378,254	232,615	475,881	806,205
1947	511,612	492,716	259,532	529,175	893,175
1948	557,402	527,137	231,294	267,118	489,762
1949	441,898	398,456	265,837	172,636	318,046
1950	558,931	715,185	106,458	363,597	768,544
1951	494,912	547,582	85,123	246,652	1,018,263
1952	687,384	690,978	132,948	123,135	564,326
1953	923,887	1,053,236	94,660	99,865	456,663

1/ Bureau of Mines. Minerals Yearbook, 1940 to 1953.
2/ Primary selenium production only, as reported by primary producers.
3/ Includes selenium dioxide and salts.

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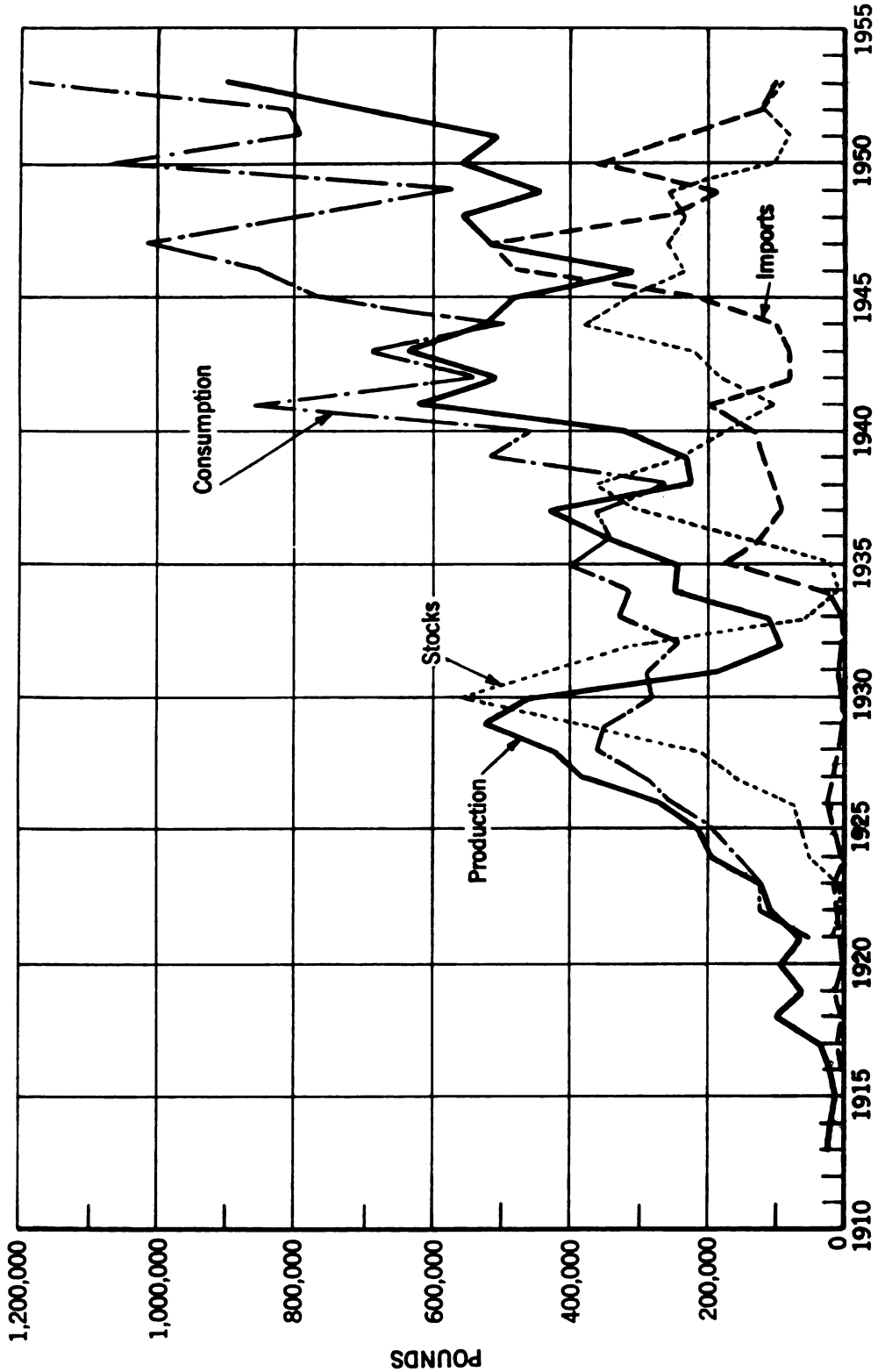

Figure 3. - United States selenium statistics.

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APPENDIX F

Selenium at Electrolytic Copper Refineries[10/]

Refinery	Se content of cu. anodes, percent	Se content of raw slimes, percent	Slime produced per ton of cu. anode, pounds	Se content of treated or leached slime, percent
A.S.R. Balt.[1]	0.061	9.65	12.5	-
A.S.R. Barber[2]	.07	7.5	16.4	10.0
A.S.R. Tacoma[3]	.035-0.051	-	17	5.3
Anaconda, G. Falls[4]	.008-0.012	3.4	5.6	4.6
Boliden[5]	.2	21.0	17.0	2.0
C.C.R., Que.	.117-0.144	18.28	16.0	5.8
Cerro[7]	.016	.64	45.0	-
E.R.S. Normal[8]	.022	2.70	20.0	-
E.R.S. High Temp.[9]	.029	2.70	20.0	-
INCO[10]	.05	13.2	8.3	20
Kennecott[11]	.047	11.59	15.0	-
Mt. Lyell[12]	.015	2.01	35.0-40.0	-
Mufulira[13]	.0014	-	2.55	-
Norddeutche[14]	.05	-	12.0	6.2-7.7
O. Oy[15]	.017	4.33	9.0-13.0	12.92
P. D. El Paso[16]	.02	-	2.0-3.0	-
P. D. Laurel Hill[17]	.02	-	5.8	-
Raritan[18]	.035-0.048	8.3	8.0	12.07
Rhodesia[19]	.0143	12.64-14.49	2.8	-
U. S. Metals[20]	.044	-	18.0	7.03

1. American Smelting & Refining Co., Baltimore, Md.
2. American Smelting & Refining Co., Barber, N. J.
3. American Smelting & Refining Co., Tacoma, Wash.
4. Anaconda Copper Mining Co., Great Falls, Mont.
5. Bolidens Gruvaktiebolag, Roonskar, Sweden
6. Canadian Copper Refiners Ltd., Montreal East, Quebec, Canada
7. Cerro de Pasco Copper Corp., Oroya, Peru
8. The Electrolytic Refining and Smelting Co. of Australia, Proprietary, Ltd., Port Kembla, N. S. W., Australia, normal
9. The Electrolytic Refining and Smelting Co. of Australia, Proprietary, Ltd., Port Kembla, N. S. W., Australia, high temperature
10. International Nickel Co. of Canada, Ltd., Copper Cliff, Ontario, Canada
11. Kennecott Copper Corp., Garfield, Utah
12. Mt. Lyell Mining & Railway Co., Ltd., Queenstown, Tasmania, Australia
13. Mufulira Copper Mines, Ltd., Mufulira, Northern Rhodesia, Africa
14. Norddeutsche Affinerie, Hamburg, Germany
15. Outokumpu Oy, Pori, Finland
16. Phelps Dodge Refining Corp., El Paso, Tex.
17. Phelps Dodge Refining Corp., Laurel Hill, N. Y.
18. Raritan Copper Works, Perth Amboy, N. J.
19. Rhodesia Copper Refineries, Ltd., Nkara, Northern Rhodesia, Africa
20. U. S. Metals Refining Co., Carteret, N. J.

10/ Modified from Butts (26).

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A comprehensive review and bibliography of the biology and geology of selenium appears in the book titled Selenium prepared by Trelease, S. F., and Beath, O. A. (177).

A booklet titled Selenium prepared by Paul Tyler (178) gives a comprehensive review of selenium as a metal of strategic importance.

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